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# Terahertz (6-15 THz) spectroscopy and numerical modelling of intermolecular vibrations in benzoic acid and its derivatives

Lucia Lepodise

*University of Wollongong*, [lml533@uowmail.edu.au](mailto:lml533@uowmail.edu.au)

Josip Horvat

*University of Wollongong*, [jhorvat@uow.edu.au](mailto:jhorvat@uow.edu.au)

R.A. Lewis

*University of Wollongong*, [roger@uow.edu.au](mailto:roger@uow.edu.au)

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# Terahertz (6-15 THz) spectroscopy and numerical modelling of intermolecular vibrations in benzoic acid and its derivatives

## Abstract

Terahertz spectroscopy of benzoic acid (BA) and two of its derivatives, 2-hydroxybenzoic acid (2OH-BA) and 3-hydroxybenzoic acid (3OH-BA), has been investigated in the spectral region 200 to 500 cm<sup>-1</sup> (6.06 to 15.15 THz). The spectra show distinct absorption features. There is agreement between some of the absorption lines observed for these compounds, despite a shift in energy, which is attributed to the differences in the molecular structures. Numerical modelling gave corresponding absorption lines, and this helped in the assignment. Temperature dependence studies revealed that most of the absorption lines are composite lines in this frequency region.

## Keywords

thz, spectroscopy, numerical, modelling, intermolecular, vibrations, benzoic, 15, acid, 6, its, derivatives, terahertz

## Disciplines

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# Terahertz (6–15 THz) Spectroscopy and Numerical Modeling of Intermolecular Vibrations in Benzoic Acid and Its Derivatives

Lucia M. Lepodise,\* Josip Horvat, R.A. Lewis

*School of Physics and Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia*

Terahertz spectroscopy of benzoic acid (BA) and two of its derivatives, 2-hydroxybenzoic acid (2OH-BA) and 3-hydroxybenzoic acid (3OH-BA), has been investigated in the spectral region 200 to 500  $\text{cm}^{-1}$  (6.06 to 15.15 THz). The spectra show distinct absorption features. There is agreement between some of the absorption lines observed for these compounds, despite a shift in energy, which is attributed to the differences in the molecular structures. Numerical modeling gave corresponding absorption lines, and this helped in the assignment. Temperature dependence studies revealed that most of the absorption lines are composite lines in this frequency region.

Index Headings: **Fourier transform infrared spectroscopy; FT-IR spectroscopy; Terahertz; THz; Vibrations; Intermolecular; Radiation.**

## INTRODUCTION

Benzoic acid (BA) has been a widely studied system, becoming a model molecule for studying the hydrogen transfer between BA molecules in the BA crystal.<sup>1,2</sup> BA molecules form dimers, bound by hydrogen bonds between their carboxylic groups.<sup>3</sup> These dimers are further bonded into crystals by weaker Van der Waals bonds. The hydrogen transfer occurs between the carboxylic oxygens within the dimers and is governed by the local crystalline fields. These fields also determine the vibrational modes of the crystal, which have been studied by the means of terahertz and far-infrared spectroscopy. Most of the intermolecular vibrational modes appear below 6 THz ( $\sim 200 \text{ cm}^{-1}$ ) and are studied by terahertz time-domain spectroscopy (THz-TDS) and waveguide techniques.<sup>4–12</sup> This work has shown that the low-frequency spectral range is useful for detecting small changes in compounds of similar molecular structures.<sup>13</sup> Numerous studies of BA spectra above 15 THz ( $\sim 500 \text{ cm}^{-1}$ ) have been reported,<sup>14,15</sup> covering mostly the intramolecular vibration modes. We focus on the intermediate range that has not been covered in the literature, between 6 and 15 THz. This range is accessible by Fourier (FT-IR) spectroscopy, which is more common and convenient than the TDS techniques. It will be shown that intermolecular modes also occur in this spectral range, allowing the studies of intermolecular interactions in molecular crystals with FT-IR. We study three systems with similar molecular structure,

which form different crystalline systems: BA, 2-hydroxybenzoic acid (2OH-BA) and 3-hydroxybenzoic acid (3OH-BA). All these compounds share a benzene ring as a common feature. Our experiments show that significant similarities are obtained in the spectra of these compounds between 6 and 15 THz, reflecting the vibrations of the benzene ring. Some of the absorption modes are identified with the help of hybrid density functional theory (DFT) modeling. This enables us to identify changes in the absorption energies due to differences in the crystalline fields and distribution of hydroxyl groups in these compounds.

Low-temperature measurements previously have been reported for BA and its derivatives.<sup>8,12</sup> However, detailed study of the temperature dependence is scarce, and it is non-existent between 6 and 15 THz, now addressed here. It is known that for many compounds, low temperatures reduce both the homogeneous and inhomogeneous broadening of spectral lines.<sup>8,12</sup> This resolves the underlying vibration features and reveals absorption lines that cannot be seen at higher temperatures. Temperature-dependent measurements thus helped identify new absorption lines. Anomalies in the temperature dependence of some of the lines were also observed, which we assign to tautomeric transitions in the crystals.<sup>1,16,17</sup> This work presents an extended terahertz database for these molecules, useful for characterization and detection applications.

## PROCEDURE

Benzoic acid and 2-hydroxybenzoic and 3-hydroxybenzoic acid were purchased from Sigma-Aldrich. The purity was 99.5% for benzoic acid and 99% for 2OH-BA and 3OH-BA. Samples were prepared by mixing 5% of powders with polyblend powder and pressing into pellets of about 0.5 mm thickness. Pressing was in a die measuring 13 mm diameter at 1.5 psi for 2 min. Polyblend is a polymer transparent in the THz region and therefore a suitable material for THz spectroscopic applications. The pellets were measured in the transmission geometry in an FT-IR spectrometer. The sample compartment was evacuated at all times to reduce effects of water vapor in the spectra. The samples were cooled in an Oxford Instruments continuous-flow helium cryostat and were measured over a wide range of temperatures. The infrared spectra were calculated for single molecules of each material using the Orca software package.<sup>18</sup> The PBE0 and the TPSSh hybrid DFT methods were used for calculation of the vibrational frequencies. The TZVPP basis set, with

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\* Author to whom correspondence should be sent. E-mail: lml533@uowmail.edu.au.

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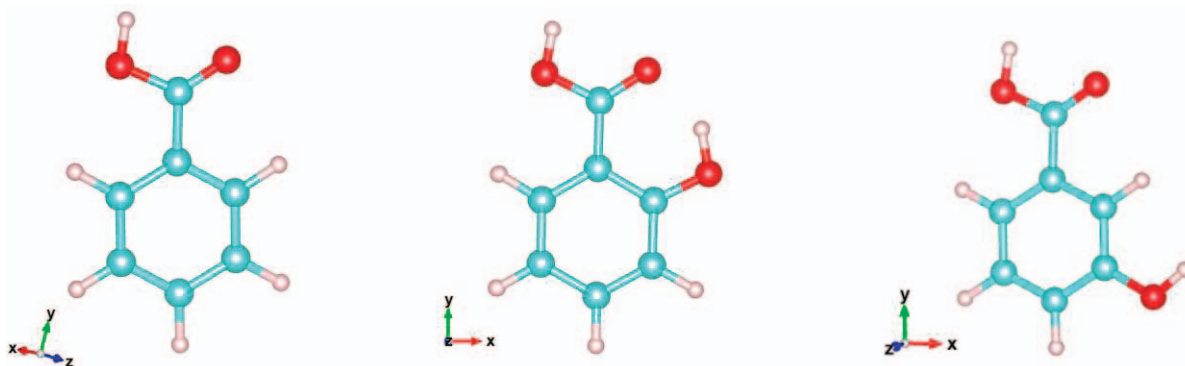


FIG. 1. Molecular structures of BA, 2OH-BA, and 3OH-BA, respectively. Cyan spheres = C, red spheres = O, and white spheres = H.

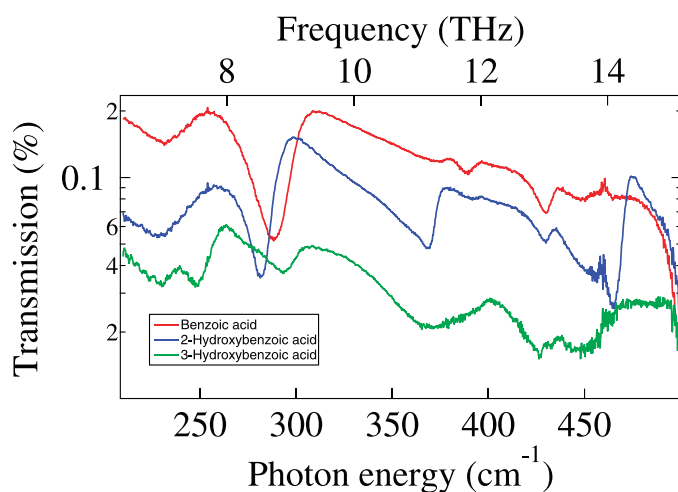


FIG. 2. Room-temperature THz spectra of benzoic acid and its derivatives.

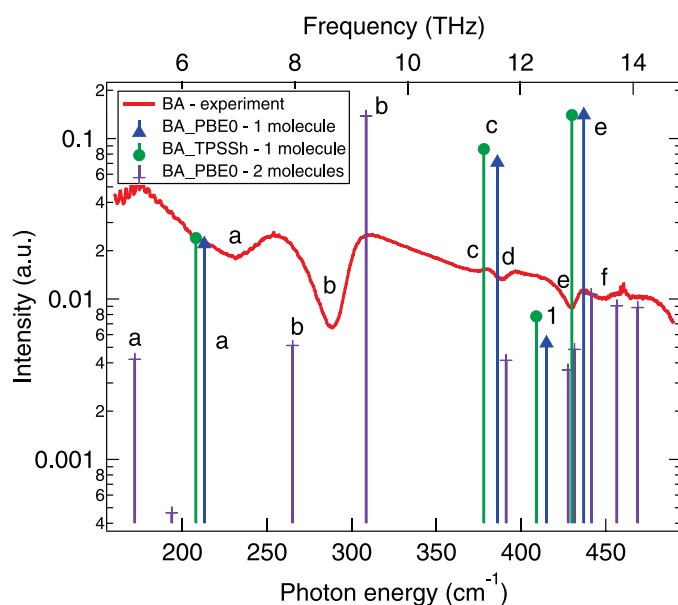


FIG. 3. Room-temperature spectrum of benzoic acid. The curve is the experimental transmission spectrum and the vertical lines give the energies and relative intensities of the emission spectra, calculated by the PBE0 and TPSSH methods for one molecule (triangles and circles, respectively). Crosses represent the numerical spectrum for BA dimer, calculated with the PBE0 method.

diffuse augmentation,<sup>19–23</sup> was used with both methods. These calculations also utilized the empirical Van der Waals correction.<sup>24</sup> In all cases the geometry was tightly optimized before frequency calculations, with the following convergence criteria: maximum energy change =  $10^{-6}$  Eh, maximum gradient =  $10^{-4}$  Eh/bohr, RMS gradient =  $3 \times 10^{-5}$  Eh/bohr, maximum displacement =  $10^{-3}$  bohr, and RMS displacement =  $6 \times 10^{-4}$  bohr.

## RESULTS AND DISCUSSION

Figure 1 shows the molecular structures of the studied compounds. There are obvious similarities but also pronounced differences between the THz spectra of these compounds with slightly different molecular structures. This discloses that, like THz-TDS, the FT-IR method is sensitive to changes in molecular structure. Figure 2 presents the room-temperature spectra of the materials studied. These exhibit broad absorption bands. The origin of the unusual asymmetry of the absorption around 11 THz is not presently understood. There is evidence for common absorption bands. The common absorption bands are shifted in energy, and this shift can

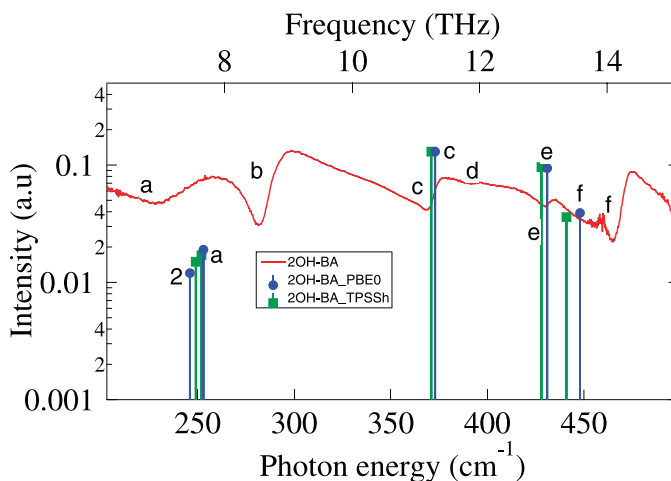


FIG. 4. Room-temperature spectrum of 2OH-BA. The curve is the experimental transmission spectrum and the vertical lines give the energies and relative intensities of the emission spectra, calculated by the PBE0 and TPSSH methods for one molecule.

**TABLE I. Common numerical modes for single molecules of BA, 2OH-BA from the TPSSh method. Both PBE0 and TPSSh gave the same vibration mode for the theoretical lines. Numbers in parentheses are the experimental absorption bands.**

Line assignment	BA cm <sup>-1</sup>	2OH-BA cm <sup>-1</sup>	3OH-BA cm <sup>-1</sup>	Description of vibration
a	208(230)	253(225)	191(229)	Symmetrical in-plane rocking of the molecule along the C1–C4 line.
c	378(365)	373(367)	364(374)	Symmetrical in-plane stretching of the molecule along C1–C4 line. Movement counteracted by the second OH in both 2OH-BA and 3OH-BA.
e	430(429)	431(429)	439(426)	Butterfly movement of the ring along C1–C4 line. Movement counteracted by the second OH and COOH in both 2OH-BA and 3OH-BA.

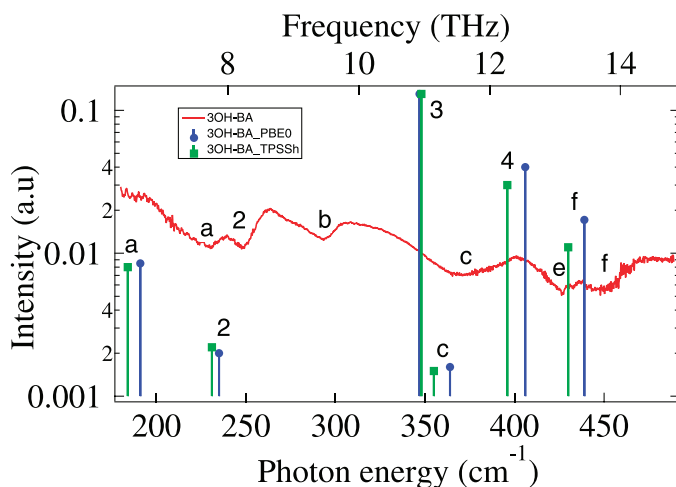
be attributed to the differences in the crystalline and molecular structures of these materials.

However, it is yet to be ascertained if the absorption bands of the different compounds appearing at similar frequencies indeed correspond to the same vibrational mode (modified by different crystalline fields and positions of the hydroxyl group). For this purpose, we compared the animated vibrations for related modes of each compound obtained from the hybrid DFT modeling.

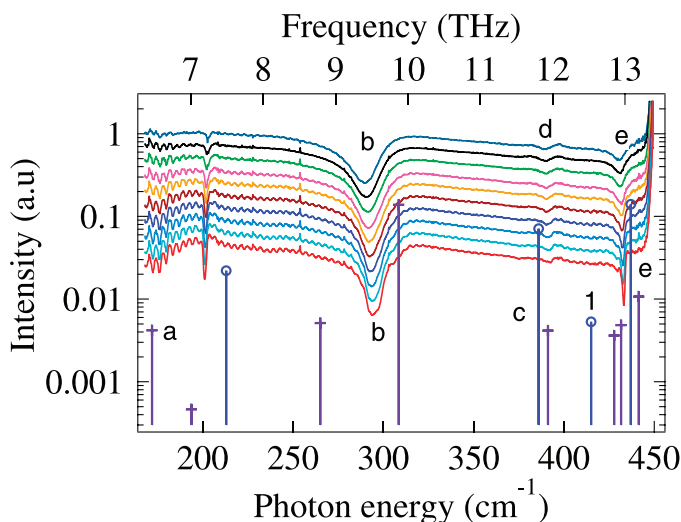
Figures 3, 4, and 5 show the comparison between the experiment and the numerical calculations for BA, 3OH-BA, and 3OH-BA respectively. The lines were assigned on the basis of the vibration modes as the main criterion, together with approximate assignment by the vibrational frequency. The energies at which the theoretical lines appear can differ substantially from the experimental ones, and this disagreement is not the same for all the lines. Because of that, only if the absorption lines calculated for the different compounds at similar frequency correspond to the same vibration mode and if their vibration frequencies match the experimental absorption bands, the experimental absorption band is ascribed to that vibration mode. Despite the energy shifts, these compounds share some observed absorption bands.

The PBE0 and TPSSh methods give equally good agreement with the experiment for individual compounds. The vibrational frequencies of DFT-based

methods typically need to be corrected by up to a few percent.<sup>25–27</sup> However, if anharmonic effects are important and are different for different absorption lines, the correction factor for each line will be different. Benzoic acid, 2OH-BA, and 3OH-BA all gave an experimental absorption band labeled “b”. This band did not have any corresponding theoretical line from the calculations of single molecules of these compounds. However, calculations for two BA molecules with the PBE0 method gave corresponding lines at 265 and 309 cm<sup>-1</sup> (8.03 and 9.36 THz) as shown in Fig. 3, both of which likely contribute to the experimental band b. They both correspond to in-plane rocking of the benzene rings, counteracted by in-plane rocking of COOH group within each molecule: with the molecules vibrating out-of-phase for the line at 265 cm<sup>-1</sup> and in-phase for the line at 309 cm<sup>-1</sup>. Modeling of single molecules did not produce a theoretical line at the frequency of the corresponding band b for any of the three compounds, yet modeling of the BA dimer produced two intermolecular lines there. Therefore, we suggest that the experimental bands b for 2OH-BA and 3OH-BA also correspond to intermolecular modes. Calculations for 2OH-BA and 3OH-BA dimers were not completed because of convergence issues. However, all three



**FIG. 5.** Room-temperature spectrum of 3OH-BA. The curve is the experimental transmission spectrum and the vertical lines give the energies and relative intensities of the emission spectra, calculated by the PBE0 and TPSSh methods for one molecule.



**FIG. 6.** Absorption spectra of benzoic acid measured at different temperatures compared to the spectrum calculated in the harmonic approximation without thermal excitations (vertical lines) for single molecule (circles) and dimer (crosses). Temperature ranges from top to bottom: 238, 211, 182, 158, 136, 116, 94, 73, 51, and 10 K. The spectra are vertically offset for clarity.



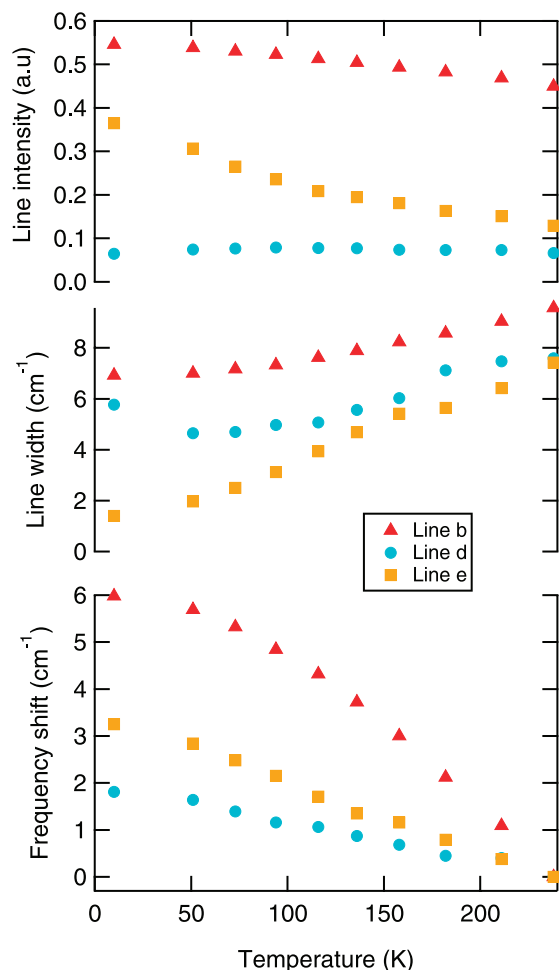


FIG. 7. Change in line frequency, width, and intensity with temperature for BA.

compounds have a similar experimental band (Fig. 2), labeled “b” in Figs. 3–5.

The theoretical lines denoted “1” for BA and “4” for 3OH-BA (Figs. 3 and 5) did not appear within the energy bounds of any of the experimental bands. The theoretical lines are shifted in energy because of approximations used in modeling. They probably describe one of the neighboring experimental bands, but it is difficult to assign these to any of the experimental bands with any reliability. The theoretical line denoted “3” in 3OH-BA is the vibration of the aromatic OH in 3OH-BA counteracted by the rest of the benzene ring and the COOH. The OH in this molecule is far from the other functional group and therefore has room to vibrate more. It is possible that this line contributes to the broad experimental band denoted “c” in 3OH-BA. On the other hand, the theoretical line denoted “4” is a result of the stretching of the ring along the C2–C4 line, with distortion of the ring and a large amplitude of H from the second OH group. This mode has been assigned to the new line emerging at low temperatures in the spectrum of 3OH-BA. The experimental bands a and 2 for 3OH-BA are reproduced theoretically (Fig. 5), with a shift to lower energies.

There is no matching theoretical line from the single-molecule calculations for the band denoted “d” that

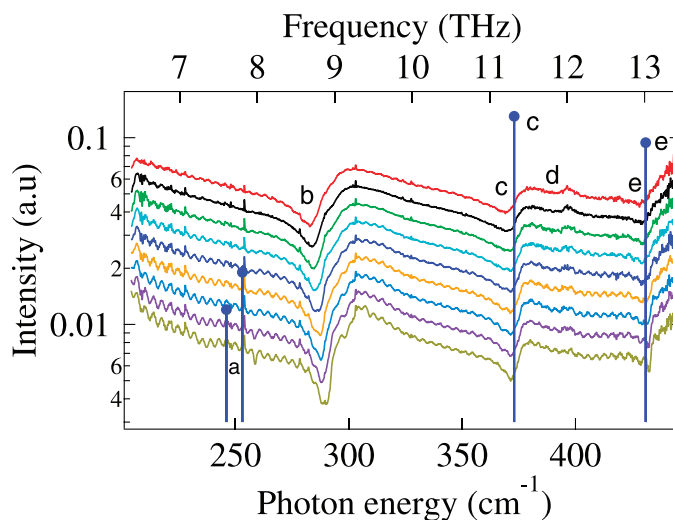


FIG. 8. Absorption spectra of 2OH-benzoic acid measured at different temperatures compared to the spectrum calculated for a single molecule in harmonic approximation without thermal excitations (vertical lines). Temperature ranges from top to bottom: 261, 232, 204, 176, 148, 121, 94, 44, and 10 K. The spectra are vertically offset for clarity.

appeared in both BA and 2OH-BA spectra. This line is probably an intermolecular mode requiring three or more molecules to model. The band denoted “f” in BA and 3OH-BA does not have corresponding theoretical lines from calculations of single molecules. The BA dimer calculations suggest that this band is associated with intermolecular interactions. It corresponds to the merger of the two lines at 457 and 469  $\text{cm}^{-1}$  (13.85 and 14.21 THz). These two lines have the same vibration mode: an in-phase butterfly motion of the benzene rings along COOH, counteracted by the COOH groups. Calculations of more than two molecules were not performed as being too demanding numerically. Table I summarizes the common peaks in all the compounds and gives their assignments. The modeling of the spectra remains a challenging task, and unambiguous assignment of experimental lines remains non-trivial.

Figure 6 shows the low-temperature spectra of benzoic acid. No extra absorption bands were resolved. The sharp band at 200  $\text{cm}^{-1}$  belongs to the polyblend filler that was not fully rationed out from our low-temperature data. The absorption band denoted “a” in Fig. 3 did not appear in the low-temperature spectra, even though there is a shoulder visible in 10 K scan. Possible reasons for the absence of band a could be experimental artifact, crystalline phase transitions with temperature change, or that band a is a “hot band”.<sup>28</sup> However, we are not aware of any evidence for the crystalline phase transitions of benzoic acid at these temperatures. The band disappears abruptly between 300 and 261 K, and it is not likely a hot band. Therefore, the most likely reason for the absence of the band a is the use of a cryostat.

The weak band labeled “c” disappeared with cooling. Bands of this nature have been previously described as hot bands,<sup>28</sup> although it is conceded the line assignment

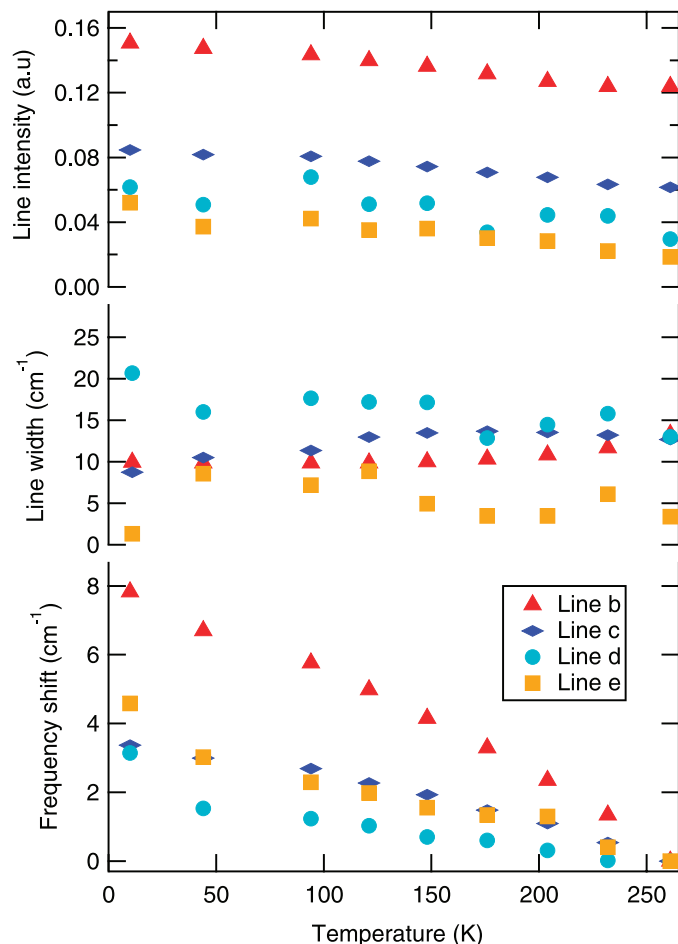


FIG. 9. Change in line frequency, width, and intensity with temperature for 2OH-BA.

may be coincidental. Most of the observed bands shifted with temperature.

Figure 7 shows change in line frequency, line width, and line intensity with temperature for benzoic acid. All the bands were red-shifted with temperature. There is a decrease in the width of lines as the sample cools. However, line d shows an anomalous line width, attributed to structural transitions of the BA molecule. BA has been found to undergo a transition from one tautomer to another. The two most stable tautomers can coexist,<sup>1,29</sup> and the temperature of the structural transition lies between 50 and 100 K.<sup>1</sup> From Fig. 7, the temperature at which the linewidth changes from the expected behavior coincides with the previously reported temperature for the structural transition of BA, thus supporting the case for structural transitions. Lines b and e show a significant change in intensity with temperature, but the intensity of line d is almost constant.

Figure 8 presents the temperature dependence of the spectrum of 2OH-BA. All the bands observed at room temperature were also observed at low temperature except for band a. A slight shoulder is observed instead, in the 10 K scan. The absence of the band a is attributed to the use of a cryostat. There is a sharp line appearing at 258  $\text{cm}^{-1}$  at 10 K, but it is hard to tell if this is real because of the oscillations observed in this spectral

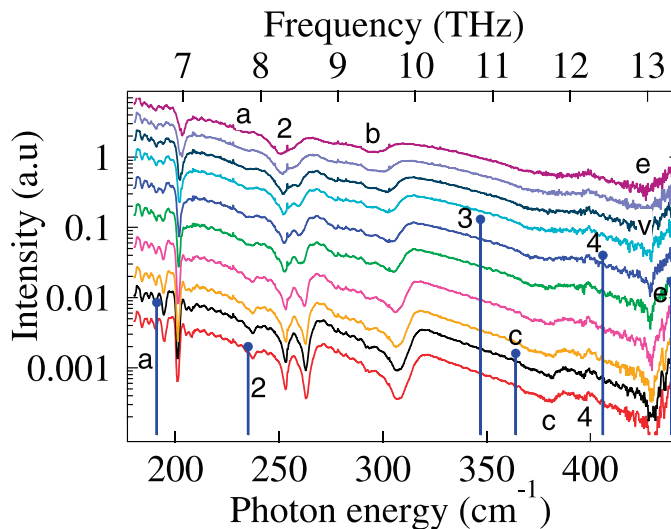


FIG. 10. Absorption spectra of 3OH-benzoic acid measured at different temperatures compared to the spectrum calculated in harmonic approximation without thermal excitations for a single molecule (vertical lines). Temperature ranges from top to bottom: 250, 210, 170, 150, 130, 110, 70, 50, 30, and 10 K. The spectra are vertically offset for clarity.

range. The behavior of the 2OH-BA lines is similar to that of the BA lines regarding the frequency shift with temperature. Figure 9 shows how the line position, width, and intensity changes with temperature. All the lines red-shifted with decreasing temperature, while the width and intensity of some of the lines were anomalous, suggesting that the lines are composite. 2OH-BA as well has been found to undergo tautomerization,<sup>16</sup> and hence, the anomalous behavior in the widths and intensities may be due to structural changes.

Figure 10 illustrates the temperature dependence of the spectrum of 3OH-BA. The prominent band at 200  $\text{cm}^{-1}$  is an artifact of incomplete rationing of the polybroad absorption band. Band a is visible, but suppressed as compared to the room-temperature measurements (Fig. 5) due to the use of a cryostat. The absorption band denoted “2” is split below 170 K. The intermolecular band b is still a prominent feature at low temperatures. An extra band denoted “4” emerges below 70 K. The band denoted “f” at room temperature (Fig. 5) was lost in the noise. Assignment of the numerical modes is shown in Fig. 10. The frequency of the assigned lines is not within the frequency range of the experimental bands, which makes this assignment somewhat tentative. However, it is based on a comparison of the vibrational modes and experimental bands between all three compounds reported here. The splitting of band 2 was not reproduced in the modeling on a single molecule.

Figure 11 shows the change in line position, width, and intensity with temperature. Most of the lines displayed a red-shift with temperature. For some the change in temperature was not systematic. Some showed an anomalous width and intensity with change in temperature. This anomalous behavior is due to the lines consisting of more lines that are not well resolved by the spectrometer. This may occur when a molecule changes from one structural configuration to the other.<sup>17</sup>

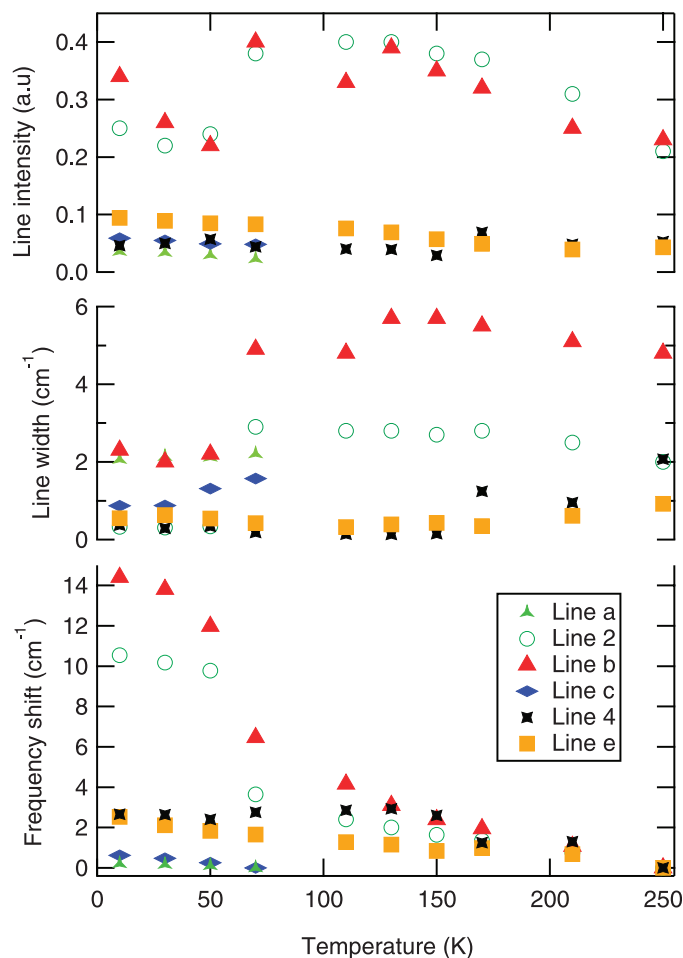


FIG. 11. Change in band frequency, width, and intensity with temperature for 3OH-BA.

## CONCLUSION

Despite the similarities in their molecular structures, BA, 2OH-BA, and 3OH-BA display different THz spectra. This shows the sensitivity of the FT-IR technique in the spectral range 200–500  $\text{cm}^{-1}$  in discerning differences between related molecules. Cooling the samples revealed features not observed at room temperature for 2OH-BA and 3OH-BA. While BA and 2OH-BA lines showed a consistent red-shift with cooling, anomalous behavior was observed for some of the 3OH-BA lines. The line width and line intensity of some of the lines fluctuated with temperature because they were not fully resolved. Despite noticeable differences in the spectra of these materials, they share some common absorption bands. In the case of the hydrogen–Van der Waals bonded systems of the nature of the ones studied here, the broadening of the vibration modes with temperature can be mainly attributed to a change in the length and strength of these bonds. This change in the bonds results in structural transitions.<sup>1,16,17</sup>

Numerical modeling was employed to understand the spectra and to assign the observed bands. The calculations revealed that the common bands were mainly due to the vibration of the benzene ring. These measurements help test the accuracy of the numerical methods. This was done by comparing the experimental results

with calculations from two different hybrid DFT methods, PBE0 and the TSSPh. Both methods were in fair agreement with the experiment, suggesting hybrid DFT calculations are useful in the interpretation of the THz spectra of BA and its derivatives.

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1. M.A. Neumann, S. Craciun, A. Corval, M.R. Johnson, A.J. Horsewill, V.A. Benderskii, H.P. Trommsdorff. "Proton Dynamics and the Tautomerization Potential in Benzoic Acid Crystals". *J. Phys. Chem.* 1998. 102(3): 325-334.
2. M. Neumann, D.F. Brougham, C.J. McGloin, M.R. Johnson, A.J. Horsewill, H.P. Trommsdorff. "Proton Tunneling in Benzoic Acid Crystals at Intermediate Temperatures: Nuclear Magnetic Resonance and Neutron Scattering Studies". *J. Chem. Phys.* 1998. 109(17): 7300-7311.
3. M. Plazanet, N. Fukushima, M.R. Johnson, A.J. Horsewill, H.P. Trommsdorff. "The Vibrational Spectrum of Crystalline Benzoic Acid: Inelastic Neutron Scattering and Density Functional Theory Calculations". *J. Chem. Phys.* 2001. 115: 3241-3248.
4. P.U. Jepsen, S.J. Clark. "Precise Ab-Initio Prediction of Terahertz Vibrational Modes in Crystalline Systems". *Chem. Phys. Lett.* 2007. 442(4-6): 275-280.
5. Z. Zheng, W. Fan, B. Xue. "Study on Benzoic Acid by THz Time-Domain Spectroscopy and Density Functional Theory". *Chin. Opt. Lett.* 2011. 9(S1): S10506-1-S10506-3.
6. Y. Ueno, K. Ajito. "Terahertz Time-Domain Spectra of Aromatic Carboxylic Acids Incorporated in Nano-Sized Pores of Mesoporous Silicate". *Anal. Sci.* 2007. 23(7): 803-807.
7. Y. Kutuvantavida, G.V.M. William, E.M. Pogson, M.D.H. Bhuiyan, K. Radhanpura, R.A. Lewis. "Material Characterization at Low Frequencies Using THz and Raman Spectroscopy". Presented at: 37th International Conference on Infrared, Millimeter and Terahertz Waves (IRMMW-THz). University of Wollongong, Wollongong, NSW, Australia; September 23–28, 2012.
8. M. Takahashi, Y. Kawazoe, Y. Ishikawa, H. Ito. "Interpretation of Temperature-Dependent Low Frequency Vibrational Spectrum of Solid-State Benzoic Acid Dimer". *Chem. Phys. Lett.* 2009. 479(4-6): 211-217.
9. H. Yan, W.-H. Fan, Z.-P. Zheng. "Investigation on Terahertz Vibrational Modes of Crystalline Benzoic Acid". *Opt. Commun.* 2012. 285(6): 1593-1598.
10. G. Min, H.-W. Zhao, W.-F. Weng, X.-H. Yu, W.-X. Li. "Substituent Effects on the Low-Frequency Vibrational Modes of Benzoic Acid and Related Compounds". *Chin. J. Chem.* 2007. 25(3): 272-277.
11. H.R. Zelsmann, Z. Mielke. "Far Infrared Spectra of Benzoic Acid". *Chem. Phys. Lett.* 1991. 186(6): 501-508.
12. N. Laman, S.S. Harsha, D. Grischowsky. "Narrow-Line Waveguide Terahertz Time-Domain Spectroscopy of Aspirin and Aspirin Precursors". *Appl. Spectrosc.* 2008. 62(3): 319-326.
13. M. Walther, P. Plochocka, B. Fischer, H. Helm, P.U. Jepsen. "Collective Vibrational Modes in Biological Molecules Investigated by Terahertz Time-Domain Spectroscopy". *Biopolymers (Biospectroscopy)*. 2001. 67(4-5): 310-313.
14. M. Boczar, K. Szczeponek, M.J. Wójcik, C. Paluszkiwicz. "Theoretical Modeling of Infrared Spectra of Benzoic Acid and Its Deuterated Derivative". *J. Mol. Struct.* 2004. 700(1-3): 39-48.
15. J. Antony, G. Von., G.M. Helden, B. Schmidt. "Anharmonic Midinfrared Vibrational Spectra of Benzoic Acid Monomer and Dimer". *J. Chem. Phys.* 2005. 123(1): 014305.
16. A.C. Maheshwari, N. Sathyamurthy, H. Mishra, H.B. Tripathi, M. Panda, J. Chandrasekhar. "Ground and Excited State Intramolecular Proton Transfer in Salicylic Acid: An Ab Initio Electronic Structure Investigation". *J. Phys. Chem. A*. 1999. 103: 6257-6262.
17. S. Clevers, F. Simon, M. Sanselme, V. Dupray, G. Coquerel. "Monotropic Transition Mechanism of m-Hydroxybenzoic Acid Investigated by Temperature-Resolved Second Harmonic Generation". *Cryst. Growth Des.* 2013. 13(8): 3697-3704.
18. F. Neese. "The ORCA Program System". *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* 2012. 2(1): 73-78.



19. R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople. "Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions". *J. Chem. Phys.* 1980. 72(1): 650-654.
20. A.D. McLean, G.S. Chandler. "Contracted Gaussian Basis Sets for Molecular Calculations. I. Second Row Atoms, Z=11-18". *J. Chem. Phys.* 1980. 72(10): 5639-5648.
21. J.-P. Blaudeau, M.P. McGrath, L.A. Curtiss, L. Radom. "Extension of Gaussian-2 (G2) Theory to Molecules Containing Third-Row Atoms K and Ca". *J. Chem. Phys.* 1997. 107(13): 5016-5021.
22. L.A. Curtiss, M.P. McGrath, J.-P. Blaudeau, N.E. Davis, R.C. Binning Jr., L. Radom. "Extension of Gaussian-2 Theory to Molecules Containing Third-Row Atoms Ga-Kr". *J. Chem. Phys.* 1995. 103(14): 6104-6113.
23. T. Clark, J. Chandrasekhar, G.W. Spitznagel, P.V.R. Schleyer. "Efficient Diffuse Function-Augmented Basis Sets for Anion Calculations. III. The 3-21+G Basis Set for First-Row Elements, Li-F". *J. Comput. Chem.* 1983. 4(3): 294-301.
24. S. Grimme. "Semi-Empirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction". *J. Comput. Chem.* 2006. 27(15): 1787-1799.
25. M.O. Sinnokrot, C.D. Sherrill. "Density Functional Theory Predictions of Anharmonicity and Spectroscopic Constants for Diatomic Molecules". *J. Chem. Phys.* 2001. 115(6): 2439-2448.
26. I.M. Alecu, J. Zheng, Y. Zhao, D.G. Truhlar. "Computational Thermochemistry: Scale Factor Database and Scale Factors for Vibrational Frequencies Obtained from Electronic Model Chemistries". *J. Chem. Theory Comput.* 2010. 6(9): 2872-2887.
27. M.A. Palafox, J.L. Nuñez, M. Gil. "Theoretical Quantum Chemical Study of Benzoic Acid: Geometrical Parameters and Vibrational Wavenumbers". *Int. J. Quantum. Chem.* 2002. 89(1): 1-24.
28. J. Barber, D.E. Hooks, D.J. Funk, R.D. Averitt, A.J. Taylor, D. Babikov. "Temperature-Dependent Far-Infrared Spectra of Single Crystals of High Explosives Using Terahertz Time-Domain Spectroscopy". *J. Phys. Chem. A.* 2005. 109(15): 3501-3505.
29. S. Hayashi, J. Umemura. "Disappearances of COOH Infrared Bands of Benzoic Acid". *J. Chem. Phys.* 1974. 60(7): 2630-2633.